

PATENT SPECIFICATION

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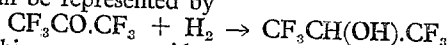
COMPLETE SPECIFICATION

Preparation of Hexafluoroisopropyl Alcohol

We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 61, Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of hexafluoroisopropyl alcohol, $\text{CF}_3\text{CH}(\text{OH})\text{CF}_3$.

The process of the invention comprises reacting hexafluoroacetone ($\text{CF}_3\text{CO}\cdot\text{CF}_3$) with hydrogen at a temperature of at least 200°C . in the presence of a catalyst comprising metallic copper and chromium oxide. The reaction believed to take place in the process can be represented by



This process provides a commercially feasible, easily controllable means of obtaining hexafluoroisopropyl alcohol which can be carried out in the gaseous phase at ordinary pressures. In general practice of the process, a mixture of vaporous hexafluoroacetone (b.p. minus 26° to minus 27°C .) and hydrogen is used at temperatures substantially in the range of 200 – 450°C .

The catalyst used in the process can be prepared, for instance by coprecipitating the hydroxides of copper and chromium by the addition to a solution of their nitrates of a solution of potassium hydroxide and filtering, washing and drying the resulting precipitate which can then be granulated, pressed into pellets or other desirable physical form. The dried material is then reduced, for instance in a stream of hydrogen while slowly raising its temperature to 300 – 350°C . To prevent excessive temperature rise due to heat of reduction, the hydrogen may be diluted with nitrogen. In the reduction the copper compound is reduced to metallic copper, and

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the chromium takes the oxide form believed to be Cr_2O_3 . If desired, the catalyst may be used on a suitable support, and conveniently the catalyst material and a support may be coprecipitated. Although calcium fluoride is preferred as the support, other supports such as other alkaline earth fluorides may be used. Spent catalyst can be reconverted to the starting materials required for catalyst preparation by digestion with nitric acid.

The ratio of metallic copper to oxide of chromium in the catalyst may vary considerably, for example from 1:1 to 5:1, preferably 1-2:1 by weight. Good results can be obtained using a catalyst comprising metallic copper and chromium oxide supported on calcium fluoride, in which the weight ratio of copper to chromium oxide is about 1-2:1, and weight ratio of copper to calcium fluoride is also about 1-2:1. The ratio of metallic copper to support can be for example from 2:1 to 1:10, preferably from 0.5:1 to 2:1.

Suitable apparatus for the process comprises preferably a tubular reactor of nickel or other suitable material such as Inconel, Monel or stainless steel (Inconel and Monel are trade marks), mounted in a furnace provided with means for maintaining the reaction zone in the reactor at the desired elevated temperature. The reactor may include inlets for introduction of controlled amounts of hydrogen and vaporous hexafluoroacetone, and may be provided with a reaction product exit connected directly to the inlet of a product recovery system.

The preferred temperature for the process is from 200 to 450°C . Although temperatures higher than 450°C . do not appear to substantially adversely affect reaction, they afford no substantial advantage. Best results appear to be obtained using temperatures from 250 to 375°C .

With regard to the proportions in which the hexafluoroacetone and hydrogen are intro-

duced into the reaction zone, the hydrogen should be present in amount at least sufficient to react with a substantial amount of the hexafluoroacetone to form a substantial quantity of the hexafluoroisopropyl alcohol. Ordinarily, hydrogen charged should amount to not less than 0.5 mol per mol of hexafluoroacetone, and equimolecular proportions or a substantial excess of hydrogen up to economic limits may be employed. For use on a large-scale, it is advantageous to adjust ratios of reactants, reaction temperatures and contact time so that the reaction products contain only a relatively small amount or substantially no unreacted hydrogen. Hence, it is desirable to charge to the reaction zone hydrogen and hexafluoroacetone in proportions of not more than about 1.5 mols of hydrogen per mol of hexafluoroacetone, and in some instances it will be found preferable to use less than equivalent proportions of hydrogen even if recycling of some of the hexafluoroacetone becomes necessary.

Contact time may be varied considerably without noticeable disadvantage to process efficiency. Generally, increasing contact time and reactor temperature results in higher reactivity. Significant conversions may be effected at contact time as short as one second, and contact times usually may lie in the range of 1—100 seconds, preferably 5—40 seconds. To a substantial extent, contact time, reactor temperature and ratio of reactants are interrelated, and optimum contact time can be determined by test runs.

While sub- or super-atmospheric pressures may be employed, the invention can be satisfactorily worked at substantially atmospheric pressure. It will be understood that in gas-phase processes of the general type described herein i.e. processes in which a gas stream flows successively through reaction and product recovery systems at what is commonly regarded as atmospheric pressure, the pressures in such systems are in fact sufficiently greater than atmospheric to effect commercially satisfactory gas flow through the apparatus. Thus, depending upon factors such as apparatus design, unpacked gas space in the reactor and desired contact time, actual pressures in systems of the kind under consideration may vary from 2 up to about 10—15 pounds gauge, (0.9 up to about 4.5—6.8 kgs. gauge) and accordingly such pressures are included in the term "substantially atmospheric pressure" as used in this specification.

The reaction products generally include hexafluoroisopropyl alcohol, unreacted hexafluoroacetone and, possibly hydrogen. The organic portion of the reaction products may be isolated by suitable cooling, for example

in a dry ice-acetone trap, to well below the boiling point of hexafluoroacetone, when unreacted hexafluoroacetone and hexafluoroisopropyl alcohol vapours condense and separate from unreacted hydrogen. Hexafluoroisopropyl alcohol may be recovered from the condensate by conventional distillation.

The following Example illustrates the invention:—

EXAMPLE

A metallic copper chromium oxide catalyst supported on calcium fluoride was prepared as follows: 167 g. of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 118. of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 75 g. of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in about 1400 ml. of water. To this solution was added a solution of 165 g. KF and 110 g. KOH in about 800 ml. of water. The resultant mixture was boiled, filtered to remove the precipitate which was then washed with water until the washings were no longer basic, substantially dried by heating in an oven at about 120°C . for several hours, and then crushed to substantially 4—14 mesh. About 250 cc. of the dried material were charged into a tubular nickel reactor about 36" (91.4 cm.) long and having internal diameter of one inch (2.5 cm.) heated externally over a middle portion of about 30" (76.2 cm.) of length by an electric furnace provided with automatic temperature control. The material was disposed in the middle portion of the reactor along about 20 inches (50.8 cm.). The material was dried by heating at a temperature up to about 300°C . in a current of nitrogen and then reduced by continued heating for about 8 hours at about 300°C . in a stream of nitrogen and hydrogen which was charged into the reactor at a rate of about 0.75 mol/hour. The finished catalyst contained by weight about one part calcium fluoride, about 1.42 parts copper metal, and about 1.2 parts chromium oxide.

This catalyst was used in the preparation of hexafluoroisopropyl alcohol as follows.

During a period of about 3 hours, a mixture of about 312 g. (1.88 mols) of hexafluoroacetone and about 4.50 g. (2.22 mols) of hydrogen were passed through the reactor, the temperature being maintained at about 300°C . Feed of hexafluoroacetone and hydrogen was such that contact time was about 14 seconds. The reaction products from the reactor were passed into a cold trap maintained at about minus 78°C . by a dry ice-acetone mixture where the organic materials condensed, yielding about 311 g. of a yellow solid. This crude material was distilled at substantially atmospheric pressure, yielding the following fractions:—

FRACTION

| | | Weight (grams) | b. pt. (°C.) |
|---|----------------------|----------------|--------------|
| A | (Hexafluoroacetone) | 51.4 | -26 to -27 |
| B | | 47.1 | -26 to +57 |
| C | | 103.3 | 57-59 |
| D | | 36.7 | 59-98 |
| E | Still bottom residue | 35.6 | — |

By chemical analysis, infrared spectroscopy, and gas chromatography, Fraction C was identified as hexafluoroisopropyl alcohol, a colourless liquid at normal conditions. Elemental analysis was: calculated for $C_3H_2F_6O$; H—1.19, F—67.86; found, H—1.20, F—66.83. The infrared spectrum confirmed the identity of the hydroxyl group at 2.72 microns, and gas chromatography showed the fraction to be more than 95% pure. The melting point was minus 10° to minus 12°C. Conversion on the basis of weight of starting material consumed was about 83% and yield of substantially pure hexafluoroisopropyl alcohol, based on the amount of starting material converted and disregarding the substantial alcohol contents of the fractions boiling immediately below and above Fraction C was about 40% by weight.

Hexafluoroisopropyl alcohol has been found to have properties which effect reduction of surface tensions of water. For example, a 2% solution of the alcohol in water reduced surface tension from about 71 to about 47 dynes. Hence, the alcohol is useful as a surfactant, for example in making emulsions of water and organic oils or solid suspensions.

WHAT WE CLAIM IS:—

1. The process for making hexafluoroisopropyl alcohol which comprises reacting hexafluoroacetone with hydrogen at a temperature of at least 200°C. in the presence of a catalyst comprising metallic copper and chromium oxide.

2. The process according to Claim 1, carried out at substantially atmospheric pressure.

3. A process according to Claim 2, in which the temperature is in the range 200 to 450°C.

4. The process according to Claim 3, in which the temperature is in the range 250—375°C.

5. The process according to any of the preceding claims, in which the hydrogen and hexafluoroacetone are charged to the reaction zone in proportions of not more than about 1.5 mols of hydrogen per mol of hexafluoroacetone.

6. The process according to any of the preceding claims, in which the weight ratio of metallic copper to chromium oxide in the catalyst is substantially in the range 1:1 to 5:1.

7. The process according to any of the preceding claims, in which the catalyst has an alkaline earth fluoride as catalyst support.

8. The process according to Claim 7, in which the ratio of metallic copper to catalyst support is from 2:1 to 1:10 by weight.

9. A process for the preparation of hexafluoroisopropyl alcohol from hexafluoroacetone, substantially as described herein.

10. Hexafluoroisopropyl alcohol when obtained by the process of any of the preceding claims.

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